Seasonal Variations in the Phosphate and Silicate Content of Sea-Water in Relation to the Phytoplankton Crop. Part V. November 1927 to April 1929, Compared with Earlier Years from 1923.

By

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With 12 Figures in the Text.

INTRODUCTION.

In the previous numbers of this series (1923, 1925, 1926, 1928) it was fully established that the phosphate and silicate content of sea-water becomes greatly reduced in spring and summer. It is possible to calculate a minimum value for the phytoplankton crop from the amount of phosphate used up, also to ascertain the production up to and between various dates; such information has a direct bearing on the supply of food for copepods and other animals upon which young fish feed. The accumulation of data of this type should in time permit of some generalization as to the favourableness or otherwise of any season with respect to the survival of relatively large numbers of young fish of various species in the locality studied. The present paper is a further contribution towards the amassing of seasonal productivity data which has been in progress since March 1923, with a gap from March to October, inclusive, during 1927. Information has moreover been sought as to the extent to which the removal of the phosphate approaches completion; the analyses of water samples low in phosphate have been carried out with a rather greater degree of accuracy than heretofore, by using a more exact method of allowing for the reagent blank, by using weaker standard solutions and by ensuring that in nearly every case the analyses were performed on the day following that on which the water samples had been taken. When the cruise extended for two days this was not possible as regards samples taken on the first day. Furthermore, measurements have been made (Poole and Atkins, 1928) of the illumination, both aerial and submarine, obtaining when the samples were taken.

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SEASONAL VARIATION IN PHOSPHATE CONCENTRATION OF WATER AT INTERNATIONAL HYDROGRAPHIC STATION E1.

The data from November 1927 to April 1929 are shown in Table 1, also records of silica content, temperature, vertical illumination, in air and at 10 and 20 m., together with the percentages of the illumination penetrating to these depths. The variation of phosphate with depth is shown in Figure 1, in which data from an earlier paper, but not previously plotted, have been incorporated. The phosphate-depth lines move to the left as the year goes on and concentration decreases. Then follows a period when the water may be almost or quite devoid of phosphate down to 20 m., while simultaneously regeneration preponderates in the deeper water. A little later active regeneration takes place at the surface,

TABLE 1.

STATION E1. The first line shows the dates on which samples were taken and top portion of the table gives phosphate results as mg. P_2O_5 per m.³, A denoting date surface and bottom. Below these are temperatures. In the lowermost section, opposite V, electrically in air. Immediately below are the percentages of the illuminations reaching refer to measurements made about midday, the values opposite V, from which they are

	1927		1928											
M	4/11	9/12	31/1	21/2	1/3	27/3	5/4	19/4	2/5	7/5	8/5	4/6	13/6	4/7
0	19†	31	431	27	33	28	24	24	10	9	9	9	4	12
5	20		35	27	26	25	25	23	10	9		9	3.5	4.5
10			36		28					10			5	4.5
15						25			10	22				3.5
20									17	18		9	5	
25						26			18	18				4
30										19		10		15
35												9	7	
40		-											10	18
50							26						14	19
70	25	31	36	28	29	41	27	23	20	19	20	13	14	25
Α	8/11	12/12	1/2	27/2	2/3	29/3	7/4	20/4	3/5	9/5	11/5	6/6	14/6	6/7
0	313	260	260	220	220	170	130	78	92				59	33
70	326	300	260	210	210	176	130	78	78			78	78	78
Α	7/11	10/12	1/2	28/2	2/3	30/3	10/4	20/4	3/5	-		6/6	18/6	6/7
0	13.4	12.1	9.1	9.7	9.7	9.6	9.8	10.1	11.4	12.5	12.4	12.1	13.1	14.1
5	13.5	11.9	9.0	9.5	9.5	9.6	9.8	10.1	11.3	12.2		11.9	13.1	13.9
10	,,	"	22	"	9.3	22	,,	**	11.1	10.9			12.7	13.6
15	,,	,,	22	,,	**	**		10.0	10.5	10.3		11.9		13.4
20	**	,,,	"	,,	,,		,,	,,	10.3	10.3		11.9	12.4	13.4
25	**	,,	,,	,	9.3	,,	9.7	"	,,	,,		11.9		13.2
30	**	**	.,	,,	"	**		10.0	10.2	10.2		11.9	12.3	11.8
40	**	,,	.,	**	**	,,		.,,	,,			11.5	11.8	11.7
70	13.5	11.9	9.0	9.5	$9 \cdot 2$	9.6	_	10.0	10.2	10.2	10.2	11.1	11.2	11.7
V		30.8			66.5	66.5	86	134		86.5		_	48.5	126
10		23%			24%	15%	21%	35%		32%	_		30%	18%
20	-	8%	_		9%	5%	6%	16%		14%			11%	4%
10		$7 \cdot 1$			16.0	10.0	18.1	47.0		27.7			14.5	22.7
20		2.5			6.0	3.3	$5 \cdot 2$	21.4		12.1			5.3	5.0

† At L4, 20 mg. surface and 22mg. bottom.

‡ At L4, 92 mg. surface and 32 mg. bottom.

as on September 22nd and October 19th, 1926, also August 16th and 29th, 1928. The vertical mixing of the water, which occurs late in September or early in October, may be followed by a diatom outburst, as shown by the decrease in the mean phosphate concentration of the column. Mixing is usually rapid throughout the isothermal column which obtains in winter, but at times regeneration may be sufficiently rapid at the surface to give markedly greater values, as on November 24th, 1926, March 21st, 1927, and January 2nd, 1929. This appears to be due to the decomposition of organic matter floating up to the surface.

In Figure 2 the phosphate data for 5 m. and bottom, 70 m.—the depth of water is about 70–73 m. actually—are shown throughout the same years. In order to avoid the irregularities introduced by surface regeneration in hot summer weather, when according to Marshall and Orr (1928)

TABLE 1 (contd.)

observations made from 1927–1929. The first column records depths in metres. The on which analyses were performed. The next portion shows silicate as mg. SiO_2 per m.³, are shown the vertical illuminations in thousands of metre candles, as measured photo-10 and 20 m. At the bottom the actual illuminations at these depths are given; they calculated, being the maxima observed for the day.

	1928								1929				
M	11/7	23/7	9/8	16/8	29/8	18/9	2/10	30/11	2/1	7/1	4/3	26/3	11/4
0	8.5	Ó	0.5	34	24	5	11	26.5	48	40	31.5	4	13.5
5	1.5	0	0	1	3.5	5	12.5	27	33.5	37	31.5	29	11.5
10	2	1.5	0	0	9			-				30	11.5
15	2	1.5	0.5	6	10	5.5							12.5
20	4	10.5	1	5.5	15	10		-	-		_		12.5
25	8.5	15	10	17		25	13					31	14
30	20	13	13	17.5	15	25							14
35													_
40	19	13					-		-				14
50		14	12	12.5	19							34.5	—
70	24	14	19	13	19	25	13	29	33.5	35.5	31.5	36	17.5
Α	12/7	24/7	11/8	18/8	30/8	19/9	4/10	1/12	4/1	9/1	6/3	28/3	12/4
0	33	59	98		120	98	163	196	183		220		_
70	78	137	130		130	210	163	196	183		228		_
Α	12/7	25/7	11/8		31/8	20/9	4/10	3/12	4/1		6/3		
0	16.1	18.2	16.6	16.0	15.9	16.8	14.9	12.1	10.5	10.0	8.5	$9 \cdot 2$	8.8
5	14.8	18.1	16.5	15.8	15.7	16.6	14.7	12.1	10.7	10.2	8.5	8.7	8.8
10	14.1	17.4	16.4	15.8	15.7	16.5	14.7					8.7	8.8
15	13.7	15.1	16.3	15.7	15.1	16.3	14.7		10.7			8.7	
20	13.2	12.7	15.9	14.9	13.6	15.5							
25	12.3	12.6	13.4	12.7	13.6	13.8	14.7	12.1					
30	11.8	12.6	13.0	12.7	13.4	13.7							
40	11.8	12.5*	12.9	12.7	12.9	13.5	14.7		10.7			-	
70	11.8	12.9*	12.9	12.9	12.7	13.5	14.7	12.1	10.7	10.2	8.5	8.6	8.8
V	130	120	56	-	111	78	65	15.3	15			_	
10	25%	47%	16%		24%	36%	16%	18%	24%				
20	6%	16%	2%		8%	16%	4%	5%	9%				
10	32.5	56.4	9.0		26.7	28.1	10.4	2.7	3.6				-
20	7.8	19.2	1.1		8.9	12.5	2.6	0.8	1.4				

* Confirmed by duplicate observations.

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the light near the surface is far too bright for effective photosynthesis by diatoms, the 5 m. values have been plotted. In July and August the surface concentrations may reach zero. The "zero" concentration really means less than 0.5 mg. P_2O_5 per m³., or quite certainly less than 1 mg. when compared most carefully with reagent blanks. Presumably



FIG. 1. Variation of phosphate concentration with depth at Station E1. The lower portion concerns 1926 up to February 1927; the upper portion concerns December 1927 to April 1929. For the sake of clearness the curves for the months have been plotted in four panels, in both upper and lower portions. Phosphate is shown as mg. P₂O₅ per m³. From data of Table 3 (Atkins, 1928) and Table 1, this paper.

it is on account of their minute size that the diatoms are so effective in removing phosphate.

The chief interest in Figure 2 lies, however, in the evidence it affords as to the date of the main spring outburst of phytoplankton, which, it may be seen, occurs much later in some years than in others. The magnitude of the crop depends upon the change in the water as a whole ; this will be considered later.

While the upper water is almost devoid of phosphate, regeneration proceeds apace in the bottom water, as shown by the peaks in the lower curve. The phosphate thus set free is gradually brought up into regions of better illumination and is used up by the phytoplankton, so that it



FIG. 2. Seasonal variation of phosphate concentration at Station E1. The upper portion gives the values at 5 m. and the lower those at the bottom, 70 m. The periods concerned are February 1926–March 1927, and November 1927–April 1929. Data for 1929 appear twice on the graphs, to compare with winter 1927 and the springs 1926 and 1928. Phosphate is shown as mg. P_2O_5 per m³. From data of Table 3 (Atkins, 1928) and Table 1, this paper.

never reaches the surface as free phosphate. Even during summer there is a slow mixing of surface and bottom water as is shown by the way the bottom temperature gradually creeps up.

SEASONAL VARIATION IN PHOSPHATE CONCENTRATION OF WATER AT INTERNATIONAL HYDROGRAPHIC STATIONS E1, E2, AND E3.

The positions of these stations are roughly as follows : E1, 10 miles S.W. of Eddystone Lighthouse; E2, Mid-Channel; E3, 7 miles W. of

TABLE 2.

Phosphate as Mg. P2O5 per M.3 and Temperatures at Stations E1, E2, and E3.

	19	927		1928								19	929			
	No	v 4		Feb. 21-22.			May 7-9.		Aug. 16-1	7.	Jan. 7.				27.	
м	EI	E2	El	Ee .	E3	E1	E2	E3	El	E2	E3	E1	E2	E1	E2	E3
0	10	22	27	11	23	9	7	10†	34	14.5	4	40	48.5	4	27.5	29
5	90	20	97	94	20	ů,	7	10+	1	0	4	37	39	29	31	26.5
10	20	50	21	24		10	8	13	Ô	ŏ	2			30	31.5	26
15						22	17	18	6	1	2					
20						18	20	25	5.5	4	26					
20	_					18	20	26	17	16	29			31		
20						10	19		17.5	16.5						
40						10	15			19.5				_		
50						-			12.5		30		_	34.5		_
60		- 08000 - 10	200.00		0000					27						
70	95		98	1		19			13			35.5		36		26
20	*	20	*	95		*	91	_	*	27		*	37.5	*	31.5	
100		*		*	25		*	28‡		*	29.5		*		*	26
0	13.8	13.4	9.7	10.2	10.3	12.5	12.3	11.9	16.0	16.9	16.6	10.1	10.6	9.2	9.4	9.8
5	13.5	13.5	0.5	0.0	10.3	12.2	12.2	11.9	15.8	16.7	16.6	10.2	10.7	8.7	9.3	9.8
10	10.0	10 0	9.5	9.9	100	10.9	12.2	11.9	15.8	16.7	16.5			8.7	9.3	9.8
15		13.5	00			10.3	10.9	11.7	15.7	16.2	16.0			8.7	9.3	
20		10.0				10.3	10.7	114	14.9	15.5	13.9					·
95		13.5	0.5	0.0	10.3	10.0	10.6	11.0	12.7	13.5	12.7					
20		10.0	00	00	10.9	10.2	10.6	11.0	12.7	13.4	12.7					
40			1.1			10 2	100			13.3	12.6					
50	10000	12.5	0.5	21 2000 - 200			10.5		12.7	13.1	12.6					
70	12.5	10.0	0.5			10.2	100		12.9		12.3	10.2		8.6		
80	*	13.5	*	0.0		*	10.5		*	13.1		*	10.7	*	9.3	
100		*		*	10.3		*	11.0		*	12.2		*		*	9.8

‡ Silica 80 mg. surface and bottom.

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Ushant. The observations at E2 and E3 are at too great intervals of time to enable one to study the changes as closely as at E1. It may be said, however, that in general conditions at E2 are much the same as at E1. There is evidence, however, that a spring phytoplankton outburst may originate at E2 before there are any signs of it at E1. Thus on February 21st, 1928, the phosphate concentration at the surface was reduced to 11 mg. at E2, and to 8 mg. half-way on towards E3. Again, on March 11th, 1926, the values 11 mg., 0 mg., 5 mg., and 7 mg., were obtained, respectively, half-way between E1 and E2, at E2, half-way on to and at E3. Also on February 15th, 1927, 13 mg. was found for E2. It may thus be seen that the rapid utilization of phosphate by the phytoplankton depends purely upon the local conditions and may arise far out at sea. It need not depend upon anything washed out from the land.

Furthermore, references are found in the literature to phytoplankton outbursts attributed by various authors to enrichment of the sea-water by river water. The latter is, however, as a rule, far poorer in both phosphate and nitrate than is sea-water in winter or early spring. In silicate alone is river water richer than sea-water, but silicate has never been shown to be a limiting factor in diatom production in sea-water, and in spring silicate is present in the sea in abundance. Pending the production of direct analytical evidence as to the correctness of this theory of enrichment by fresh water, the author is unwilling to regard it as correct, save in comparatively landlocked basins.

Station E3 may be low in phosphate down to 15 m., but the deeper colder water is never greatly depleted, since there is so much vertical mixing thereabouts and the depth is considerably greater than at E1 or E2.

The Rapid Regeneration of Phosphate in Winter and the Water of an Offshore Wind.

Rough weather prevailed before and after Christmas 1927, but on January 2nd, 1928, it seemed just possible to get to E1 for routine water samples and to measure submarine illumination in mid-winter. Now it so happened that a rather unusual condition was observed, there was a steep gradient in phosphate concentration along the inshore stations, from L1 near the Laboratory to E1, 22 miles out.

The water at the Breakwater, L2, was just three times as rich in phosphate as that at E1; one might have concluded that the fresh water was enriching the sea-water, but this obviously required that the seawater at L2 must have been diluted with fresh water to a very great extent, the salinity at E1 being $35 \cdot 34^{\circ}/_{\circ\circ}$, rather a high value typical of Atlantic water. It was found, however, that even at L1 the salinity was $30.29^{\circ}/_{\circ\circ}$.

TABLE 3.

Phosphate as Mg. P_2O_5 per M³., Phosphate in Stored Samples, Temperatures and Salinity in Parts per Thousand. Between January 2nd and 7th, 1929, the Prevailing Wind was Offshore, mainly from N.E. At the bottom of the Table Silicate Analyses are shown as Mg. SiO₂ per M³.

Jan.	m.	L1	L2	L3	L4	L5	L6	E1 N	Mid E1-E2	E2
2†	0	161	143	125	125	93	125	48		
2	5					_		33.5		
2	70	<u> </u>						33.5		
79	0	-		39	49.5	48	48	40	49	48.5
7	5				35		36	37	37	39
7	10			34						
7	25	* ~	*	34						
7	40			*	34					
7	60				*	*	34.5	-		
7	70						*	35.5	36	37.5
			PB	IOSPHATE	IN STO	DRED SA	MPLES.			
9+	0			360	210	150	59	16**		
-+	0			000	510	100	52	40		
<u></u>				Т	EMPERA	TURE.				
2	0	8.9	8.5	9.4	10.2	10.3	10.6	10.5	10000	
7	0			8.8	9.6	9.7	9.9	10.1	10.3	10.6
7	5			9.2	9.6		9.9	10.2	10.4	10.7
7	В	_		9.7	9.9		10.1	10.2	10.4	10.7
				S	ALINITY	0/				
0	0	20.20		~	AND ALL A	, 100.		05 0 11		
2	0	30.29	-	1	0= 10	0= 10	05.00	35.34*	1	
1	0				35.18	35.19	35.33	35.37	35.41	35.36
7	. 5			34.78	35.13		35.23	35.37	35.35	35.33
7	В			35.03	35.21		35.28	35.35	35.35	35.37
					SILIC	А.				
2	0	870‡‡	686^{++}_{++}	466	246	190	217	183		

† Jan. 2nd analysed Jan. 4th. ¶ Jan. 7th analysed Jan. 9th. ‡ Jan. 2nd analysed again on Jan. 9th. ** 70 m. sample gave 37 mg. * Bottom reached before depth indicated. †† Isohaline column. B, denotes bottom. ‡‡ Subject to a correction for tint in water, but as they stand they agree well with results in Table 1 of Atkins, 1926, p. 92, when latter are corrected by new factor.

This remarkable phosphate gradient was, moreover, shown to be a surface phenomenon only at E1 on January 2nd.

Between January 2nd and 7th the prevailing wind was offshore, mainly from the N.E. Under these conditions the fishermen at Plymouth say that it is almost useless to fish, as nothing worth while is caught. The idea prevails that the water is then very clear. On January 2nd photo-electric measurements did not show any exceptional clearness, and at E1 the Secchi disc could only be seen 9 m. down, as against a

maximum of 22 m. The 9-m. value is probably somewhat low, perhaps even as much as 3 m.-for the sea was very rough, with a heavy easterly swell. It was thought that the high phosphate concentration near the coast would give an indication as to whether surface water was being blown out to sea and replaced by deeper water moving nearer inshore. Accordingly on January 7th, the weather being exceptionally cold, temperature, phosphate and salinity depth series were worked from L3 to E2, as shown in Table 3. From L4 to E2 the surface phosphate was closely the same, save for E1, which was lower. Furthermore, the whole water column was somewhat richer at E2 than at the stations nearer land. Again the salinity results show a uniform Atlantic water from E1 to E2, and at L6, surface, with only very slight dilution, 3 parts in 1000 at L6. 5 m., and very little more at L4 throughout the watercolumn. There is therefore no evidence whatever that any extensive movement of the surface water was occasioned by the prevailing offshore wind or that the high values for phosphate in the surface waters were in any way connected with the wind. They arose through the decomposition of material rich in phosphate floating up to the surface all over the area studied, though the possibility is not precluded that a certain amount of seaweed and particulate matter may drift out to sea through wind action. Further evidence of enrichment through decomposition is offered by the fact that certain of the water samples taken on January 2nd and stored till January 9th gave even higher values than when freshly drawn.

A Comparison of the Phosphate Content of the Water at E1 in Different Years.

In Table 4 the mean values of the phosphate content of the watercolumn are shown, from 1923–1929. There is usually a maximum in January. For the seven years the mean maximum was $35\cdot1$ mg., varying from $37\cdot0$ to $31\cdot0$ mg. Very strangely there were mid-winter phytoplankton outbursts in mid-December 1925 and late December 1926.

The minimum values for the water-column were found in June, July, or August, with secondary minima in April or May. For the five summers studied the mean minimum was 7.6 mg., varying from 8.7 to 5.1 mg.

The data are shown in Figure 3, the years being continued into the January following to show the winter maxima or depressions. The most striking thing about the curves, apart from their general similarity, is the rapid fall in the spring of each year. The fall, however, differs from year to year both as regards its date and its rate, as shown by the slope of the curve. Tables 5 and 6 have been prepared to facilitate the comparison of the years, as indicated in their headings. The dates are shown at which certain phosphate concentrations were reached at

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TABLE 4.

Phosphate Content of the Water-Column, Surface to Bottom, 70 m., at Station E1, expressed as Mg. P_2O_5 per M³. The months are divided into three portions each equal in length

		1923	1924	1925	1926	1927	1928	1929
Jan.	Ι		37.0			21.6		36.5
"	II			31.9	40.0*			
"	III				_	36.2		
Feb.	Ι				33.0			
,,	II		32.0	31.1		27.9	27.8	
"	III						-	
Mar.	Ι	37.0			36.4		28.5	31.5
"	II	-	$22 \cdot 1$	28.3		29.0		
,,	III			-			25.8	31.4
April	Ι		15.0				25.6	
,,	II				9.5		23.1	14.4
,,	III	27.7		8.5				
May	Ι						17.2	
,,	II		12.1	9.2	12.9			
,,	III	11.6						
June	Ι			15.8			10.6	
,,	II	13.2	9.1				8.3	
,,	III				16.0			
July	Ι		8.7	6.9	10.5		13.7	
"	II	7.4		_			14.2	
"	III						10.2	
Aug.	Ι		10.1	19.2			9.4	
,,	II	16.1			10.4		12.0	
,;	III						15.3	
Sept.	I		16.1	5.1				
,,	II	13.9					19.0	
,,	III				8.6			
Oct.	Ι		14.9	18.2			12.8	
,,	II	16.0			18.2		1.0	
. ,,	III					·		
Nov.	Ι	20.0				23.5		
,,	II		20.1	25.9		a		
,,	III				25.6	· · · · ·	27.9	
Dec.	Ι		32.0			31.0		
,,	II	34.0		18.6	29.8			10000
••	III		1 (<u>1 - 1)</u>		21.6		34.0	

* This is really a surface value for L6, but L3–L6 gave the same value for phosphate, but it may possibly be too high for E1. Weather was too bad to get to E1 or to do the depth series.

surface and bottom, also the temperatures of the water on those dates. Both dates and temperatures are then compared with those of the first year of the series, 1923. Now the phosphate depletion is a measure of





the phytoplankton production, which is only secondarily affected by temperature. The latter has been included mainly on account of its influence upon the rate of hatching of fish eggs and upon the rate of growth of animals.

TABLE 5.

DATES AND TEMPERATURES WHEN CERTAIN PHOSPHATE CONCENTRATIONS WERE REACHED AT E1, SURFACE. TAKING THE 1923 DATES AND TEMPERATURES AS ARBITRARY STANDARDS THE ADVANCES OR RETARDATIONS OF THE OTHER YEARS ARE RECORDED IN DAYS AND DEGREES.

mg.	1923	1924	1925	1926	1927	1928	1929	1924	1925	1926	1927	1928	1929
30	March 30	Feb. 18	Feb. 25	Feb. 3	Feb. 6	Feb. 13	March 18	41	33	55	52	46	12
30	9.7°	$8 \cdot 4^{\circ}$	9.6°	9.5°	$9 \cdot 2^{\circ}$	9.5°	8.9°	-1.3°	-0.1°	-0.2°	-0.5°	-0.2°	-0.8°
20	April 28	Feb. 28	March 20	March 21		April 22	April 4	59	39	38	·	6	24
20	10.2°	8.0°	9.4°	9.7°		10.4°	9.0°	$-2\cdot 2^{\circ}$	-0.8°	-0.5°		$+0.2^{\circ}$	-1.2°
10	May 10	April 28	April 6	April 10		May 2	April 13	12	34	30		8	27
10	11.0°	9.4°	9.5°	10.2°	_	11.4°	8.8°	-1.6°	-1.5°	-0.8°		$+0.4^{\circ}$	$-2\cdot 2^{\circ}$
2.5	May 21	June 18	April 18	July 21		July 6		-28	33	-61		-46	
2.5	11.4°	13.7°	9.7°	17.0°		14.7°		$+2\cdot3^{\circ}$	-1.7°	$+5.6^{\circ}$		$+3.3^{\circ}$	
2.5	Sept. 15	Aug. 24	Sept. 10	Sept. 6		Aug. 25		+22	5	+9		+21	
2.5	15.0°	15.0°	16.0°	16.9°		16.0°		0.0°	$+1.0^{\circ}$	$+1.9^{\circ}$		$+1.0^{\circ}$	
10	Sept. 28	Oct. 20*	Oct. 6	Oct. 3		Sept. 28		-22	-8	-5		0	
10	14.0°	12.9°	14.3°	15.9°		15.5°		-1.1°	$+0.3^{\circ}$	$+1.9^{\circ}$		$+1.5^{\circ}$	
20	Nov. 7†	Nov. 22	Nov. 11	Nov. 6	Nov. 6	Nov. 5		-15	+6	-1	-1	-2	
20	$12 \cdot 2^{\circ}$	12.3°	12.6°	13.3°	13.7°	13.6°		$+0.1^{\circ}$	$+0.4^{\circ}$	$+1.1^{\circ}$	$+1.5^{\circ}$	$+1\cdot4^{\circ}$	
30	Dec. 1	Dec. 6	Jan. 2§	Dec. 12	Dec. 3	Dec. 14		-5	-32	-11	-2	-13	
30	10.9°	11.9°	10.2°	11.7°	$12 \cdot 1^{\circ}$	11.4°		$+1.0^{\circ}$	-0.7°	$+0.8^{\circ}$	$+1.2^{\circ}$	$+0.2^{\circ}$	10.0000
		* Also on S	ept. 2, giving	s + 26.	† Als	o on Oct. 11.	ţ	Also on 1	Dec. 21.	ş	1926.		

TABLE 6.

DATES AND TEMPERATURES WHEN CERTAIN PHOSPHATE CONCENTRATIONS WERE REACHED AT E1, BOTTOM. TAKING THE 1923 DATES AND TEMPERATURES AS ARBITRARY STANDARDS, THE ADVANCES OR RETARDATIONS OF THE OTHER YEARS ARE RECORDED IN DAYS AND DEGREES.

mg.	1923	1924	1925	1926	1927	1928	1929	1924	1925	1926	1927	1928	1929
30	April 14	Feb. 20	March 17	March 17	March 21	Feb. 17	April 1	54	28	28	24	57	13
30	9.6°	8.6°	$9 \cdot 2^{\circ}$	9.5°	9.0°	9.4°	8.7°	-1.0°	-0.4°	-0.1°	-0.6°	-0.2°	-0.9°
20	May 9	March 17	April 11	March 27		May 2	April 9	53	28	43		7	30
20	10·2°	8·0°.	. 9·4°	9.5°		10.2°	8.8°	$-2\cdot 2^{\circ}$	-0.8°	-0.7°		0.0°	-1.4°
15	May 20	April 9	April 26	April 2 [†]		May 25	April 14	41	24	48		-5	36
15	10.4°	8.3°	9.5°	9.5°		10.8°	8.9°	$-2\cdot1^{\circ}$	-0.9°	-0.9°		$+0.4^{\circ}$	-1.5°
15	Oct. 20*	Aug. 15	Sept. 19§	Oct. 6‡		Oct. 988		66	31	14		+11	
15	$13 \cdot 2^{\circ}$	$12 \cdot 1^{\circ}$	13.0°	14.6°		14.4°		$-1\cdot 1^{\circ}$	-0.2°	$+1.4^{\circ}$		$+1.2^{\circ}$	
20	Nov. 6	Nov. 4	Sept. 29	Oct. 18		Oct. 28		2	38	19		9	
20	12.3°	12.9°	13.5°	14.5°		13.5°		$+0.6^{\circ}$	$+1\cdot2^{\circ}$	$+2\cdot2^{\circ}$		$+1.3^{\circ}$	
30	Dec. 1	Dec. 4	Dec. 28		Dec. 3	Dec. 8		-3	-27		-2	7	
30	11.0°	11.9°	10.5°		$12 \cdot 2^{\circ}$	11.8°		$+0.9^{\circ}$	-0.5°		$+1.2^{\circ}$	$+0.8^{\circ}$	
	* Also June 4 and July 27. † Also July 4						‡ Also May	18.		§ Also M	ay 20 and	July 19.	
			**	Max, 27 mg.	Dec, 13,		§§ Also July	7 24 and A	ug. 14.				

It may be seen that 1924, 1926 and 1929 are early years, 1928 being late, with 1923 even later. The differences are, moreover, very striking since 1924 and 1926 are 6 to 7 weeks ahead of 1923 and 1928. The earliest spring, 1924, happened also to be the coldest, both at the time of the vernal outburst and in general. It must accordingly have been



FIG. 4. The production of phytoplankton, at Station E1, may be deduced from the uprights above the zero line; in reality these lines show the difference in the mean phosphate concentration of the water-column, expressed as mg. P_2O_5 per m³., between two successive observations. Decrease in phosphate, being equivalent to production of phytoplankton, is shown above the zero line. From data of Table 3 (Atkins, 1926).

[Reprinted from Fig. 4, Jour. Mar. Biol. Assoc., 1926, 14, 454.]

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one in which the hatching of fish eggs went on most slowly. This year therefore should be an outstanding one as regards suitability or otherwise for various species of young fish. The next year to 1924 as regards low temperature was 1929, a moderately early year, though not as early as 1924 or 1926—or even as 1925 as regards the surface.

The autumnal regeneration of phosphate seems to proceed rather more



FIG. 5. Similar to Fig. 4, but for years 1926-1929, spring. From data of Tables 4 and 7.

regularly as to date and temperature than does the vernal consumption process.

It is possible to make further use of the data of Table 4, which gives the mean phosphate concentration of the water-column, because the differences between consecutive values are a measure of the consumption or regeneration of phosphate. Such differences are shown in Figures 4 and 5 as perpendiculars above or below the zero line, erected at distances on the abscissæ corresponding to the date of the second of each pair of analyses.

In comparing these two figures it is obvious that the height of a perpendicular depends to some extent on the frequency of the observations. The diversity of the years is, however, brought out very clearly. Thus the two late years, 1923 and 1928, are in some respects quite different; 1928 began as a rather early year but did not maintain its productivity; 1924 began very early and its further progress, both as regards production of phytoplankton and regeneration of phosphate, was monotonously regular. In 1925 large outbursts were followed by periods of very considerable regeneration; both 1925 and 1926 had December outbursts; 1926 and 1929, as well as 1925, had single spring outbursts of remarkable magnitude.

During 1928 analyses were performed at shorter intervals in connection with the work on illumination. It may be seen in Figure 5 that the first perpendicular above the line is followed by a very small one below it, the second above the line by a third above it, but very small. There are further on two very small perpendiculars below the line in May and July. Obviously the rates of production of phytoplankton varied greatly. Table 7 shows such rates in terms of consumption or regeneration of phosphate, the latter being denoted by a plus sign; these were obtained as described in the heading of the table, and are shown in Figure 6, the construction of which is given in the legend.

The phenomenon that is brought out most clearly in Figures 4, 5, and 6 is that production of phytoplankton is not a process that proceeds uniformly at a slow rate, or at an ever-increasing rate, till limited by lack of phosphate. Such a deficiency does ultimately limit it, but in between productivity proceeds in a series of bounds, with periods of no change of rate or with periods of decay in between. Since phosphate consumption is never very great below 25 m. at E1, in the absence of vertical mixing, this depth has been selected as one above which the main region of photosynthesis lies. The illumination at 25 m. is from about 1.0 to 10.4 per cent of full daylight. Vertical mixing, however, introduces complications, especially as the main spring outburst occurs before the formation of the epithalassa. Moreover, in autumn, at the end of September or very early in October, the resumption of vertical

TABLE 7.

The Upper Portion of the Table shows Phosphate Concentration, in Mg. P_2O_5 per M.³, at Station E1, Averaged from 0–70 M., also from 0–25 M. and 25–70 M., together with the Differences, \triangle , Between Consecutive Observations. The lower portion gives the Intervals between the Observations, the Rates of Phosphate Consumption or Regeneration, in Mg. P_2O_5 per M.³ per Day, and the Mean Dates for which the Rates are taken as Applicable.

Date.	4/11/27	9/12	31/1/28	21/2	1/3	27/3	5/4	19/4	2/5	7/5	4/6	13/6
0–70 m.	23.5	31.0	36.2	27.8	28.5	$25 \cdot 8$	25.6	$23 \cdot 1$	17.1	17.3	10.6	8.3
Δ		+ 7.5	+ 5.2	- 8.4	+ 0.7	-2.7	- 0.2	- 2.5	- 6.0	+ 0.2	- 6.7	-2.3
0-25 m.	21.0	31.0	36.5	27.4	$28 \cdot 1$	25.4	24.9	23.2	12.2	14.5	9.0	4.5
Δ.		+10.0	+ 5.5	-9.1	+ 0.7	-2.7	- 0.5	- 1.7	-11.0	+ 2.3	- 5.5	- 4.5
25–70 m.	24.9	31.0	36.0	27.9	28.7	26.0	27.0	23.0	19.9	19.0	11.5	11.1
Δ	—	+ 6.1	+ 5.0	- 8.1	+ 0.8	- 2.7	+ 1.0	-4.0	-3.1	-0.9	-7.5	-0.4
Interval, days		35	53	21	9	26	9	14	13	5	28	9
Mean date		21/11	4/1	10/2	25/2	14/3	31/3	12/4	25/4	4/5	21/5	8/6
Rate, 0-70 m.		+0.21	+0.10	-0.40	+0.08	-0.10	-0.02	-0.18	-0.46	+0.04	-0.24	-0.26
Rate, 0-25 m.		+0.29	+0.10	-0.43	+0.08	-0.10	-0.06	-0.12	-0.85	+0.46	-0.20	-0.50
Rate, 25–70 m.	_	+0.17	+0.10	-0.39	+0.09	-0.10	+0.11	-0.29	-0.24	-0.18	-0.20	-0.04
					TADLE	7 (andina						
					TADLE	(commu	ca).					
4/7 $11/$	7 23	/7 9/	8 16/8	29/8	18/9	2/10	30/11	2/1/29	7/1	4/3	26/3	11/4
13.7 14.2	2 10-	·2 9·	4 = 12.0	15.3	19.0	12.8	27.9	34.0	36.5	31.5	31.4	14.4
+ 5.4 + 0.6	$5 - 4 \cdot$	0 - 0	8 + 2.6	+ 3.3	+ 3.7	- 6.2	+15.1	+ 6.1	+ 2.5	-5.0	- 0.1	-17.01
4.8 3.6	$6 4 \cdot$	·2 1·	3 7.6	11.4	8.1	12.4	27.0	35.0	37.3	31.5	27.4	12.3
+ 0.3 - 1.2	2 + 0	·6 – 2·	9 + 6.3	+ 3.8	-3.3	+ 4.3	+14.6	+ 8.0	+ 2.3	- 5.8	- 4.1	-15.1
18.6 20.	1 13	·6 13·	8 14.4	17.4	25.0	13.0	28.3	33.5	36.0	31.5	33.7	15.6
+ 7.5 + 1.4	5 - 6	5 + 0	2 + 0.6	+ 3.0	-7.6	-12.0	+15.3	+ 5.2	+ 2.5	- 4.5	$+ 2 \cdot 2$	-18.1
21 7	1:	2 17	7 7	13	20	14	59	33	5	56	22	16
23/6 7/	7 17	7 31/	7 12/8	22/8	8/9	25/9	31/10	16/12	4/1	4/2	15/3	3/4
+0.26 + 0.07	7 - 0.3	3 - 0.0	5 + 0.37	+0.25	+0.18	-0.44	+0.26	+0.19	+0.50		-0.05	-1.06
+0.01 - 0.17	7 + 0.0	-0.1	7 + 0.90	+0.29	-0.17	+0.31	+0.25	+0.24	+0.46	-0.10	-0.19	-0.94
+0.36 + 0.2	1 - 0.5	54 + 0.0	1 + 0.09	+0.23	+0.38	-0.86	+0.26	+0.16	+0.50	-0.08	+0.10	-1.13

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mixing may cause the upper 25 m. to show a gain in phosphate, indicating apparently a period of regeneration, whereas the whole water-column may show a reduction in phosphate, as on October 2nd, 1928. For these reasons, the values for the whole column are the most reliable, though the other two have been tabulated for the information they can yield



FIG. 6. The ordinates represent mg, P_2O_5 per m³, per day, and denote the rates of change in phosphate concentration at Station E1, throughout the whole 70 m. water-column. The rates are plotted for the dates midway between those on which the water was sampled. Decrease in concentration, being equivalent to increase in phytoplankton, is plotted above the zero line. The crests are therefore times of maximal rates of production of phytoplankton, the troughs of maximal rates of decay of phyto- and zoo-plankton combined. From data of Table 7.

when considered in relation to the possible sources of error in their interpretation. The maximum consumption rate found for the whole column was 1.06 mg. P_2O_5 per m.³ per day, for April 3rd, 1929, followed by 0.46 for April 25th, 1928, 0.44 for September 25th, 1928, and 0.40 for February 10th, 1928. Such rates would soon reduce the phosphate content to zero were they to be continued. For the upper 25 m. the

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maxima were 0.94 for April 3rd, 1929, 0.85 for April 25th, 1928, 0.50 for June 8th, 1928, and 0.43 for February 10th, 1928. The greatest rate of all was observed in the lower region, 25–70 m., when vertical mixing was active, namely, 1.13 mg. for April 3rd, 1929, followed by 0.86 for September 25th, 1928, and 0.54 for July 17th, 1928.

The writer is indebted to Mr. H. W. Harvey for the construction of isohalines which show that there was no marked influx of water into the mouth of the English Channel during the period studied. It is accordingly legitimate to regard the cyclic processes at E1 as being those taking place in a closed system.

A COMPARISON OF THE VARIATION IN HYDROGEN ION CONCENTRATION, TOTAL CARBON DIOXIDE AND PHOSPHATE CONTENT OF SEA-WATER.

An extended series of measurements of the hydrogen ion concentration was made some years ago in order to obtain an estimate of the minimum weight of the phytoplankton crop from the change in the carbon dioxide content as shown by alteration in alkalinity. This was abandoned as the phosphate analyses gave the desired information more simply. It was intended, however, to institute a comparison of the two, but a few series only could be made in 1928. These are shown in Table 8, besides similar observations for 1922. When arranged in order of the monthly dates the two years are seen to agree closely, as might be expected if made in the same year.

TABLE 8.

Hydrogen Ion Concentration, pH value, of Sea-water at Station E1, Determined Colorimetrically at Sea upon freshly drawn Samples using Cresol Red and McClendon's Buffer Solutions. Comparison of Autumn 1922 with 1928.

m.	Sept. 18th, 1928.	Sept. 22nd, 1922.	Oct. 2nd, 1928.	Oct. 12th, 1922.
0	8.24	8.22	8.22	8.20
5	8.24	8.22	8.22	8.20
10	8.23	8.22		8.20
15		8.21	8.22	8.20
20	8.21	8.21		8.20
25	8.19	8.20	8.22	8.20
30	8.15	8.18	·	8.20
40	8.15	8.18		8.20
70	8.14	8.18	8.22	8.20

A comparison of the changes in phosphate and in carbon dioxide is shown in Figure 7, constructed as indicated in the legend. It may be

seen the vernal fall in carbon dioxide and in phosphate are rather similar, both are reduced during the summer, and rise in winter, though the high value of the previous winter was not reached by the carbon dioxide by January 1924. The figure makes it clear that though the phosphate is greatly reduced, in summer, throughout the whole water-column—to



FIG. 7. The left-hand ordinates denote cubic centimetres of carbon dioxide per litre, those on the right mg. of P_2O_5 per m³. The phosphate values are those for the whole water-column for the period shown by the abscissæ. The carbon dioxide values, broken line, denote the total amount present in the water-column, in c.c. per litre—the water being of alkaline reserve "26," namely, requiring 26 c.c. of N/10 HCl to neutralize one litre at 100° C. The carbon dioxide was found by converting the pH (logarithmic) values obtained, with cresol red and McClendon's standards (Atkins, 1924), into concentrations, cH values, for each depth, and from these a mean value for the water-column was got and converted into the pH value. From the pH values for the various dates, McClendon's (1917) curve for excess base 26 was used to read off the c.c. of CO_2 per litre. Author indebted to H. W. Harvey for this figure.

about 25 per cent of its winter value, yet the reduction in carbon dioxide is comparatively small, from 47.8 to 46.5 c.c. per litre.

The Silicate Content of Sea-water and its Seasonal Variation.

Table 1 shows the silicate at Station E1, expressed as mg. SiO_2 per m³. The results have been plotted in Figure 8, surface full line and bottom broken line. For comparison a dotted curve shows phosphate, at 5 m. There is a general agreement between the curves, but the silicate curve never reaches zero. It does, however, reach a minimum of 33 in July,

which is about the limit of what is definitely detectable by the method. The surface silicate is, during the summer, rather lower than the bottom concentration. The sudden rise in the latter in September is probably associated with movement of water in from slightly further out. Of this there is definite hydrographic evidence. It is also noteworthy that whereas the phosphate one winter is closely the same as that in the following winter, when at its maximum, yet the 1928–1929 silica concentration was far below that of 1927–1928. Furthermore, in April 1928 the steep fall in silica took place some weeks before the marked fall in phosphate. This looks as if the latter was due in the main to a Phæocystis





outburst, and the later complete exhaustion of phosphate, when silica was increasing, may possibly have been due largely to the growth of Peridinians. In the absence of a proper examination of the plankton it is impossible to decide such questions.

Table 3 furnishes additional support to the finding of a previous year as to the steep silicate gradient existing near the land.

THE PHYTOPLANKTON AT STATION E1.

Lack of a collaborator has rendered it impossible to make regular and approximately quantitative observations on the phytoplankton and to correlate them with the changes in phosphate concentration as Marshall

and Orr (1927) have done in the Clyde. It was found, however, that Phaeocystis globosa occurred abundantly in the tow-nets on May 2nd, 1928, the date on which the fall in phosphate concentration was also found (Table 1), temperature 10.2-11.4° C. On April 4th, 1929, every sample of water obtained by the Nansen-Pettersen bottle from surface to bottom contained Phæocystis in abundance. This also coincided with the



FIG. 9.—Mean monthly sunshine records, in hours per day, for England S.W. (including S. Wales), plotted for 15th of each month, 1923-1925. From Meteorological Office Records.

[Reprinted from Fig. 5 of Jour. Mar. Biol. Assoc., 1926, 14, 457.]

sudden fall in phosphate, which took place about a month earlier than in 1928, the temperature being 8.8° . Next in abundance to Pheocystis the water from the sample bottles, examined directly, without centrifuging, with a low power in a small dish, contained the following : Lauderia borealis, abundant; Rhizosolenia stolterfothii, a fair amount; Chætoceros decipiens, frequent; Nitzschia delicatissima, embedded in the jelly of Phæocystis, a small species of Gymnodinium; Navicula membranacea, also occasional cells of Rhizosolenia shrubsolii, R. robusta, Skeletonema

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costatum, Chætoceros densus, C. sociale, Navicula sp., Nitzschia closterium, Streptotheca tamensis, Hyalodiscus stelliger, Thalassiosira sp., Pleurosigma sp., Peridinium ovatum, P. pentagonum, Dinophysis sp., Spirodinium spirale. The water-column being isothermal the plankton was





well distributed but seemed more abundant at 15 m. than elsewhere. The phosphate concentration was slightly lower at 5 and 10 m. than elsewhere. I am indebted to Dr. M. V. Lebour for kindly identifying the phytoplankton.

The Causes of the Difference in the times of Phosphate Consumption from Year to Year.

In an earlier paper (1926) it was shown that the years 1924 early, 1925 intermediate, and 1923 late were arranged in the order of their early spring sunshine records, as may be seen in Figure 9. A similar agreement had been found by Herdman, Scott and Dakin (1910), 1907 having an unusually early diatom crop, following, with a lag, a high value for February sunshine. Marshall and Orr (1927), however, found a remarkable constancy in the date of the vernal outburst in the Clyde area. Their phosphate estimations were checked by counting the diatom chains, a good agreement being found. In another paper (1928) the E1 observations concerning the years 1923, 1924 and 1925 were shown to be associated with predominant north-sector winds in 1924. The relation works back to the sunny weather and clear skies associated with northerly winds.

Figure 10 is similar to Figure 9, but concerns 1926–1929; 1926 has been classed as an early year, like 1924, but Figures 4 and 5 show that in detail the years were very different, for 1924 gave a regular series of productivity uprights, whereas in March 1926 regeneration preponderated, being associated with 2.8 hours sunshine per day. The big outburst came in April, with an average of 5.2 hours sunshine per day. After this 6 hours daily in May and 8 hours in June did not lead to the complete exhaustion of the phosphate, though the surface values were further reduced. The epithalassa having become established regeneration took place, but very low phosphate values were found in July, August and September, even with decreased sunlight. One has, however, to consider the possible effect of variations in the clearness of the water, data on which are recorded in Table 1 and are shown in Figure 11. These variations are such as to alter the illumination about eight times, much the same as is found between a dull winter day giving 15,000 metrecandles and a very bright summer or spring day with 120,000 m.c. So unless one knows the absorption coefficient it does not follow that a period of bright sunshine is necessarily one of high illumination at, say, 15-25 m., though it will probably be so at depths down to 10 m. in the open sea.

The year 1927 should have been an earlier year than 1926, with 3.9 hours daily sunshine for March. Observations up to March 21st, after which they are lacking, showed no outburst, but rather slow regeneration till March, following upon the small and unusual outburst at the very end of December 1926.

The year 1928 was studied in great detail. There was a moderate outburst late in February with small ones in the end of March and middle

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of April and larger ones early in both May and June, causing the year to be grouped with 1923 as late, though it began well in February; in this month the sunshine was 116 per cent of the normal, January having had 125 per cent. That for March was only 73 per cent, and April 89 per cent.



FIG. 11. The upper portion represents the percentage of the vertical illumination (received on a horizontal surface) penetrating to 10 and 20 metres, at Station E1, on the dates shown. The lower portion gives the vertical illuminations, in 1000-metre-candles, in air, at 10 and at 20 m. Data from Poole and Atkins (1929).

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In 1929 the most striking feature was the great outburst early in April. After an almost normal January sunshine (104 per cent) and only 75 per cent of the normal in February, that for March had risen to 165 per cent, 6.54 hours per day. This seems obviously connected with the early April outburst. Figure 11 also shows the mean monthly length of the day for the meteorological district, namely, England S.W. and



FIG. 12. The lowermost curve shows the length of day in hours for the meteorological district England S.W. (including S. Wales). The upper full curve shows the normal "effective" length of day for the district, counting each hour of sunshine as equivalent to two hours of diffuse light. (See text.) The curve with dot and dash shows the "effective" length of day for 1928; the curve with dashes only represents 1929.

S. Wales. It is obvious that length of day is a very important factor as regards the causation of an outburst of plant growth. Poole and Atkins (1929) found that the vertical illumination due to the sun's direct rays is about twice as great as that due to the diffuse light. Thus sunshine, which usually occurs in the midday hours, has the effect as it were of trebling the duration of the light, when at its highest, for in addition to a normal diffuse light of, say, 30,000 m.c. there will be an extra 60,000 due to sunlight; this is equivalent to three times as long at 30,000 m.c. Since, however, the sunshine hours are already included in the length of the day we can get a rough idea of the "effective length of day" by adding, to the mean length for the month, twice the mean monthly sunshine for the month of the year under consideration. This gives an approximate relative figure for the same months of different years; thus for March the normal "effective" length of day is 19.7 hours for the district, whereas that for 1928 was 17.6 and for 1929 it was 24.9 hours. The comparison is only a rough one, however, for the different months, because the average diffuse illumination varies greatly from month to month; also the sunlight is not twice as powerful as the diffuse light in the depth of winter and is more than twice as powerful in mid-summer. Figure 12 shows the mean monthly length of day for the district, also the normal "effective" length of day, obtained from the normal values of the mean monthly sunshine. The broken lines show the "effective" length of day for 1928 and 1929. The great difference in March appears to offer a rational explanation of the remarkable phytoplankton outburst early in April 1929. Pending the obtaining of accurate measurements of the daily or monthly illumination in metre-candle hours by means of a permanently exposed photo-electric cell and a Cambridge Instrument Co. "thread recorder," the curves of Figure 12 may serve as a rough approximation.

ESTIMATION OF SILICATE.

As mentioned previously (1923, 1926) there is always a suspicion that a trace of silicate may dissolve from the bottle unless this has been waxed. The values given were obtained for the most part using samples from waxed bottles, but these were occasionally supplemented by analyses from the ordinary hard green glass bottles. The following values, in mg. SiO_2 per cubic metre, were obtained for E1, September 18th, 1928, analysed on 20th: 0 m., 99; 15 m., 100; 20 m., 102; 25 m., 163; 30 m., 118; 40 m., 144; 60 m., 209. Only the 0 m. sample was from a waxed bottle, but obviously the 15 and 20 m. samples agree well. The 25 m. sample is from water totally different as regards temperature and phosphate, but from this depth downwards both are almost uniform, whereas the silicate values are not. It seems possible that suspended

diatom tests and siliceous material has been dissolved in varying amount, but the glass risk is not excluded; the tints are moreover so faint that too great reliance must not be placed in the analytical results. The degree of accuracy attainable may be judged from the following analyses of samples from E1, July 23rd, 1928, using waxed bottles: taking 100 mg. and 200 mg. standards the surface results were 55 and 60 mg. respectively and the bottom 142 and 130 mg. Nevertheless, it seems likely that such accuracy is not always obtained.

A matter of greater importance is the picric acid used in making up the standard solution, for which 36.9 mg. of picric acid has been taken as corresponding to 50 mg. p.l. of SiO₂ in solution as silicate according to Diénert and Wandenbulcke (1923). Thresh and Beale (1925) used 40 mg. of picric acid. King and Lucas (1928), however, state that 25.6 mg. of vacuum-dried, C.P. picric acid per litre gives a colour equivalent to 50 mg. p.l. of SiO₂ with the reagents. They suggest that possibly the earlier workers neglected to dry the picric acid, to which water is usually added for safety. My own standard solution was made from picric acid crystals which had been for several years in a nearly empty bottle and appeared to be quite dry; they were further dried over sulphuric acid in a desiccator. The crystals used by Thresh and Beale were also dried over sulphuric acid in an ordinary desiccator (private communication). It seems unlikely that so large a discrepancy can be accounted for merely by the difference in drving in an ordinary and a vacuum desiccator, yet the work of King and Lucas, carried out with every precaution and with picric acid recrystallised from benzene (Benedict, 1922), renders it desirable that the standards used by different workers should be compared till uniformity is secured.

As first pointed out by Folin and Doisy (1916), impure picric acid, specially common at about that time, may be a source of error in estimating creatine and creatinine. A rather laborious purification gave a product that could be relied upon, though Benedict (1922) reported samples that were not even improved by this repetition of recrystallization of sodium picrate from water. Benedict found that recrystallization of even the "technical" grade of picric acid from hot benzene gave a product which was quite satisfactory. The impurities give a deep colour with alkali; this is important in the creatine estimation, but affects the silica estimation far less, since it is carried out by comparison with an acid mixture. Recently, however, Benedict (1929) has found samples of picric acid which show little improvement after crystallization from benzene. He recommends the use of glacial acetic acid as a solvent for the dried picric acid, or alternatively recrystallization of the sodium salt by a modification of the Folin-Doisy method, using sodium carbonate instead of sodium hydroxide.

Through the courtesy of Dr. E. J. King it is now possible to be sure that analyses on opposite sides of the Atlantic are truly comparable. He examined my standard picric acid solution and found that it agreed exactly with his own, made up to be 36.9 mg. per litre. This, according to Diénert and Wandenbulcke, is equivalent in colour to one containing 50 mg. SiO₂ per litre. According to King and Lucas this is matched by 25.6 mg. of picric acid per litre. Apparently the fault lies in the picric acid originally used by Diénert, for the silica content of silicate can readily be checked by gravimetric analysis. Since in my earlier work I used Diénert and Wandenbulcke's factor, all the figures published must be multiplied by 1.30. Those given in this paper are now correct by King's standard.

Methods of Calculating the Allowance to be made for the Reagent Blank.

The analyses of phosphate were made, as heretofore, by the coeruleomolybdic method of Denigès, using 100 c.c. of liquid in a Hehner tube. The allowance for the reagent blank is of course a perfectly general correction, necessary in all colorimetric work involving minute quantities.

The blank correction was formerly made as follows: if using as standard a 0.05 mg. per litre solution of phosphate, reckoned as P_2O_5 , or 50 mg. per cubic metre, 100 c.c. of distilled water plus reagents matches 10 c.c. of standard plus reagents. The amount of the blank then corresponds to $\frac{50 \times 10}{100}$ =5. This amount corresponds to a full column, therefore if an unknown solution matches at a reading of 40, it is clear that the standard column contains two-fifths of the blank in excess of its supposed phosphate content, whereas the unknown contains the full amount of reagents producing the blank. Accordingly three-fifths of the blank must be subtracted from the apparent amount found for the unknown, namely,

 $\frac{50 \times 40}{100}$ =20, less 3=17.

This, however, is not quite correct, for the real strength of the standard has been increased by the presence of the reagents also. In general terms let k denote the true amount of the blank, c the concentration of the standard before addition of the blank-producing reagents, x the reading for the blank and y that for the unknown solution containing an amount z: then

$$\begin{array}{l} \mathbf{k}{=}(\mathbf{c}{+}\mathbf{k}){\times}\frac{\mathbf{x}}{100} \ ,\\ \text{and } \mathbf{z}{+}\mathbf{k}{=}(\mathbf{c}{+}\mathbf{k}){\times}\frac{\mathbf{y}}{100} \end{array}$$

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Now taking, as before, x=10 and y=40, with c=50 mg. per cubic metre, we get :—

$$100 \text{ k}=500+10 \text{ k}$$
, hence $\text{k}=5.5$

and
$$z+k=\frac{55\cdot5\times40}{100}=22\cdot2$$

hence z=16.7, as against z=17 by the approximate correction. In view of the fact that a difference of two units on the scale corresponds to 1 mg. per cubic metre, the use of the approximate correction is not a cause of any appreciable error. However, using a weaker standard solution the error may become more serious, especially for higher values of k and lower values of y.

Thus, with k as before, viz. 5.5, y=40 and c=25, we get

$$z+k=\frac{30.5\times40}{100}=12.2$$

whence z=6.7 and the approximate method gives :---

$$z = \frac{c \times 40}{100} - \frac{60}{100} k,$$

hence z=10-3=7, which is in good agreement. However, with x=24, and c=25 we get $k=6\cdot0$ by the approximate method and 7.9 by the exact one. With these values and y=30 the approximate method gives $3\cdot3$, the exact $2\cdot0$. An alternative approximation, in cases where y approaches to x, is to subtract and calculate from :—

 $z = \frac{(y-x)c}{100}$, which with the above assigned values gives z=1.5, which

would then be rounded off to z=2 as obviously nearer than z=1.

Since in the present paper the interest lies partly in seeing how near to complete exhaustion the phosphate content may go, it has seemed advisable to use the first approximate method when c=50, as before, and to adopt the exact formula for use with the very weak solutions estimated with standard c=25 mg. per cubic metre.

SUMMARY.

1. The phosphate content of sea-water at Station E1 ranged, during the period November 1927–April 1929, from 48 mg. P_2O_5 per m³., to 0.0 mg. The former was an exceptional and temporary surface value during phosphate regeneration in mid-winter; the latter was a very usual value at from 0–15 m. during July, August or even September.

2. For the whole water-column, 0-70 m., at E1 the maximum values were 36.2 and 36.5 mg. during the winters 1927-1928 and 1928-1929 respectively. The minimum value for the column was 8.3 mg. in June 1928.

3. For the seven years 1923-1929 the maximum value for the phosphate content of the whole column was 37.0 mg. in 1923 and 1924, the lowest winter maximum observed being 31.0 mg. For the seven years the mean maximum value was 35.1 mg. The five summers gave a mean minimum value of 7.6 mg. for the column, the absolute minimum being 5.1 mg. on August 31st, 1925.

4. Additional evidence has been obtained that the surface may be a region of phosphate regeneration, not only in winter, but in bright summer weather when apparently the illumination is too intense for diatoms to thrive. Normally the bottom and deeper waters are the chief sites in which regeneration becomes apparent.

5. Taking the vernal consumption of phosphate as a standard, the years 1924, 1926 and 1929 were early years, 1928 being late with 1923 even later. The differences may amount to as much as 6 or 7 weeks. The earliest spring, 1924, happened also to be the coldest. It must accordingly have been one in which the hatching of fish eggs went on most slowly. This year, therefore, should be an outstanding one as regards suitability or otherwise for various species of young fish.

6. The differences in the seasonal productivity of the various years is well brought out by erecting perpendiculars, at the proper positions on the time abscissæ, which are proportional to the differences between successive observations of the phosphate concentration of the watercolumn. It is seen that the production of phytoplankton, as measured by phosphate consumption, proceeds by a series of outbursts.

7. The rate of production throughout the whole water-column was as much as 1.06 mg. P_2O_5 per m³. per day for April 3rd, 1929. For the upper 25 m, the maximum rate found was 0.94 mg, for the same date, with 1.13 mg, for the column from 25–70 m. Owing to vertical mixing with surface water poorer in phosphate this rate is fictitiously the greatest.

8. A comparison of the total carbon dioxide content of the watercolumn at various times during the year has shown that in a general way the minimum is reached at about the same time as the phosphate minimum. The carbon dioxide content was found to vary from 47.8to 46.5 c.c. per litre, so it never remotely resembles complete exhaustion in the open sea.

9. There is a general agreement between the curves for seasonal variation in phosphate and in silicate, but the latter never reaches zero. The July minimum for the surface, 33 mg. SiO_2 per m³. is very near the limit of what can be detected. The winter maxima differ more than do the phosphate max ma from year to year, that for 1927–1928 and 1928–1929 being respectively 320 and 220 mg. A sharp fall in silica content in the spring may be several weeks ahead of a similar fall in phosphate.

10. The factor for silica determination as given by King and Lucas has been adopted in preference to that of the originators of the method of colorimetric comparison against picric acid. This necessitates the multiplication of the results of my analyses, published heretofore, by the factor 1.30. The trouble has apparently been due to the presence of an impurity in the picric acid used by Diénert which may render advisable a method of purification recognised as necessary in the determination of creatine and creatinine.

11. In April 1929 a sudden fall in phosphate concentration was accompanied by a remarkably rich phytoplankton outburst. Every sample of water bottled from 0–70 m. contained lumps of Phæocystis jelly, as well as the diatom *Lauderia borealis* in abundance, though not so in every sample. *Rhizosolenia stolterfothii, Chætoceros decipiens*, and *Nitzschia delicatissima* were also plentiful; twelve other species of diatoms were found and four of the Peridineæ.

12. The order in which the years stand in § 5 is, in a general way, the order of spring sunshine. The variations in the clearness of the water must be taken into account in assessing the submarine illumination; such variations may cause an eight-fold variation in the upper 20 m., much the same as is found between winter and spring.

The length of the day as well as the sunshine is important in regulating the amount of photosynthesis. Crediting the day with two hours extra daylight for each hour of sunshine a graph has been constructed which shows how 1929 was in this respect ahead of 1928 in the spring. The comparison is a fair one for the same months of different years, but only rough for the different months, as the sun's altitude varies.

It should be added that the values quoted for the salinity of the water were determined in the Government Chemists' Laboratory, London.

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